

Performance Improvement of the All-Lead Redox Flow Battery in Fluoroboric Acid Electrolyte

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Abstract

The performance of the all-lead redox flow battery was enhanced by using stainless steel as the negative electrode and tantalum carbide (TaC) as the positive electrode in an intermixture of $\text{Pb}(\text{BF}_4)_2\text{-HBF}_4$ aqueous electrolyte. The results of cyclic voltammetry (CV) measurements show that stainless steel and TaC electrodes are capable of offering higher voltage efficiency than graphite electrodes at a lower scan rate. In the charge-discharge cycles, the battery was charged at current densities of 10, 20 or 40 $\text{mA}\cdot\text{cm}^{-2}$ with a charge capacity of 7.0 $\text{mAh}\cdot\text{cm}^{-2}$ and discharged down to 1.0 V at the same current density. The miniature battery offers an average discharge voltage of 1.55 V, an average coulombic efficiency of above 96%, and an energy efficiency of above 65%. The battery in 1.5 $\text{mol}\cdot\text{L}^{-1}$ of $\text{Pb}(\text{BF}_4)_2$ + 1.0 $\text{mol}\cdot\text{L}^{-1}$ of HBF_4 aqueous solution is able to deliver an average energy efficiency of above 80% at the current density of 10 $\text{mA}\cdot\text{cm}^{-2}$.

Keywords

All-lead Redox Flow Battery; Tac Electrode; Lead Fluoroborate; Fluoroboric Acid

Introduction

In recent years, several new power storage systems have been proposed such as supercapacitors, lead-acid batteries, and the sodium-sulphur fused batteries [1, 2]. Redox flow battery is labeled as the most ideal one among the new storage systems in virtue of their special advantages [3]. A number of redox flow batteries have been fabricated, such as Cr/Fe [4-6], V [7, 8], Zn/Br₂ [9, 10], polysulfide/Br₂ [11], etc. Most of the batteries require the employment of ion-exchange membranes. However, such membranes are expensive, leading to an increase in the complexity and cost of the cell, while simultaneously introducing cross-contamination of reactive species through the ion-exchange membrane [12, 13]. Pletcher proposed a lead-acid redox flow battery

based on the Pb^{2+}/Pb and $\text{PbO}_2/\text{Pb}^{2+}$ couples in methanesulfonic acid where the lead methanesulfonate is highly soluble and there is no requirement for a membrane [12-19]; this reduces the cost of the batteries significantly. However, it is a pity that the energy efficiency is still low, only around 65% ($\sim 20 \text{ mA}\cdot\text{cm}^{-2}$) [13].

On the basis of the literatures [12-19], a novel all-lead redox flow battery employing graphite as both positive and negative electrodes in a fluoroboric acid aqueous solution is proposed [20], which offers an energy efficiency of above 74% ($10\sim 20 \text{ mA}\cdot\text{cm}^{-2}$). In this paper, stainless steel as the negative electrode and tantalum carbide (TaC) as the positive electrode for the all-lead redox flow battery are compared with graphite electrodes in the intermixture of $\text{HBF}_4\text{-Pb}(\text{BF}_4)_2$ aqueous electrolyte, and the performance of the battery is improved. The miniature battery in 1.5 $\text{mol}\cdot\text{L}^{-1}$ $\text{Pb}(\text{BF}_4)_2$ + 1 $\text{mol}\cdot\text{L}^{-1}$ HBF_4 can offer a maximum energy efficiency of above 80.2% at the current density of 10 $\text{mA}\cdot\text{cm}^{-2}$.

Experimental

All solutions were prepared with distilled water. Chemicals of analytical grade purity were used. Fluoroboric acid (40 wt%) and lead (II) oxide (99.0%) were provided by Xilong Chemistry Engineering Corporation. The lead fluoroborate was formed by using the reaction between lead (II) oxide and fluoroboric acid. In the electrolytes, the concentration of the lead (II) oxide was 0.1 $\text{mol}\cdot\text{L}^{-1}$, 0.5 $\text{mol}\cdot\text{L}^{-1}$, 1.0 $\text{mol}\cdot\text{L}^{-1}$ or 1.5 $\text{mol}\cdot\text{L}^{-1}$, and the concentration of free HBF_4 was kept as 1.0 $\text{mol}\cdot\text{L}^{-1}$.

The TaC was prepared as follows. The phenol-formaldehyde resin used here was novolac type

(Tianjing Resin Factory) and was mechanically mixed with hexamethylene tetramine (Xilong Chemistry Engineering Corporation). The mixing ratio was set at 10:1 by weight. Both sides of Ta foil with a thickness of 0.2 mm were coated with a slurry formed by mixing the above mixture with ethanol and heated in an oven at 150°C in air for 1 hr. The Ta foil coated with solidified resin was heated to 850°C at a rate of 5°C·min⁻¹ by using a pipe furnace, held there for 1 hr and then allowed to cool naturally. Nitrogen gas was used during the temperature-programmed calcinations. After cleaning the carbons from the surface, the obtained TaC foil was then used as a working electrode. The crystalline information of the TaC was determined by X-ray diffraction (XRD), distinct diffraction peaks of Ta (JCPDF card 4-788) and TaC (JCPDF card 35-801) phases were present, indicating TaC crystallites were coated on the surface.

Cyclic voltammetry (CV) measurements were carried out using a Solartron 1280Z workstation in a three-electrode configuration assembly consisting of pure lead as the counter-electrode, TaC, graphite or stainless steel as the working electrode, and Ag/AgCl (saturated KCl aqueous electrolyte) as the reference electrode. The electrolyte for CVs is 0.1 mol·L⁻¹ Pb(BF₄)₂+1.0 mol·L⁻¹ HBF₄. The surface area of all the working electrodes is 2.0 cm × 2.0 cm.

The galvanostatic charge–discharge tests were carried out in a two-electrode cell with a LAND CT2001A battery test system (Jinnuo Wuhan Corp., China). The experimental battery was constructed with TaC as the positive electrode and stainless steel as the negative electrode with an interelectrode gap of 5 mm. The electrolytes used here are solutions of 0.5 mol·L⁻¹, 1.0 mol·L⁻¹ and 1.5 mol·L⁻¹ Pb(BF₄)₂ in 1.0 mol·L⁻¹ HBF₄. The cell charge–discharge current densities were 10, 20 and 40 mA·cm⁻² with a charge capacity of 7 mAh·cm⁻² and a continual discharge of 1.0 V cut-off, and then cycled at about 50 cycles to determine the stabilized efficiency. All the cells described in this paper were tested in the same stir condition with a magnetic stirrer.

Results and Discussion

Fig. 1 represents the CV curves recorded on TaC and graphite as the positive electrode in 0.1 mol·L⁻¹ Pb(BF₄)₂ + 1.0 mol·L⁻¹ HBF₄ at scan rates of 1, 5 and 10 mV·s⁻¹ in the potential range of 0.7–1.75 V. The voltammograms are similar to those reported by many

workers for the deposition and reduction of PbO₂ in other acid media and references therein [12]. For the cycle of 5 mV·s⁻¹ and 10 mV·s⁻¹ scan rates recorded on the TaC positive electrode (see Fig. 1(a)), it is clear that nuclei of PbO₂ remain on the surface even after the scan up to 0.7 V and, in the circumstance of 1 mV·s⁻¹, the current densities and charges for both PbO₂ deposition and dissolution are relatively large. Comparing with the curves in Fig. 1(a) and (b), at the potential scan rate of 1 mV·s⁻¹, anodic peak and cathodic peak on the TaC electrode appear at 1.60 and 1.09 V, those peaks on the graphite electrode appear at 1.62 and 1.11 V. But the peak deposition current density on the graphite electrode is lower than that on the TaC electrode, and the potential gap between nucleation and dissolution on the graphite electrode is higher than that on the TaC electrode. Therefore, using TaC as the positive electrode may have higher voltage efficiency at low charge–discharge rates. As the scan rate increases, the deposition current density on both the graphite and the TaC electrodes increases though the peak deposition potential on the TaC electrode shifts to more positive potential. This indicates that using TaC as the positive electrode may have lower voltage efficiency at high charge–discharge rates.

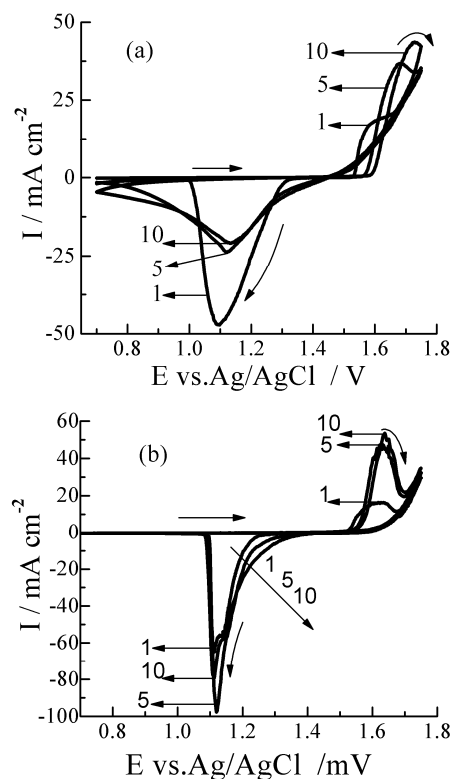


FIG. 1 CYCLIC VOLTAMMOGRAM CURVES RECORDED ON BOTH TAC AND GRAPHITE AS POSITIVE ELECTRODES AT DIFFERENT SCAN RATES IN THE ELECTROLYTE OF 0.1 MOL·L⁻¹ Pb(BF₄)₂+1.0 MOL·L⁻¹ HBF₄, (a) ON TAC, (b) ON GRAPHITE

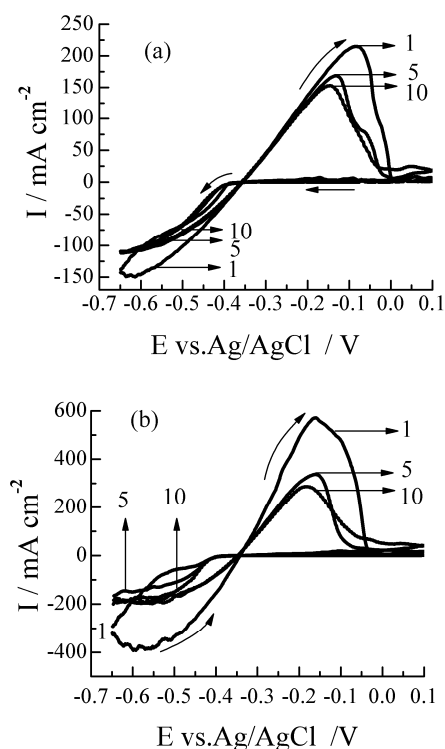


FIG. 2 CYCLIC VOLTAMMOGRAMS RECORDED ON BOTH STAINLESS STEEL AND GRAPHITE AS NEGATIVE ELECTRODES AT DIFFERENT SCAN RATES IN $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Pb}(\text{BF}_4)_2 + 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HBF}_4$, (a) ON STAINLESS STEEL, (b) ON GRAPHITE

Fig. 2 reports CV curves recorded on stainless steel and graphite as the negative electrode in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Pb}(\text{BF}_4)_2 + 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HBF}_4$ in the potential range of $-0.65 \sim 0.1 \text{ V}$. On the scan towards more negative potentials, on the stainless steel electrode (Fig. 2(a)), a reduction wave is observed below -400 mV . The wave shows a well-defined limiting diffusing current plateau and the plateau shift to more negative value as the scan rate increases. On the reverse scan at a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$, a cathodic peak appears, attributing towards electrochemical and diffusion controlling. The reduction process continues to -350 mV , and the current immediately becomes anodic before an anodic peak is observed. This is the classical response for the deposition and stripping of Pb onto a foreign substrate and the kinetics of the Pb^{2+}/Pb couples are rapid. In Fig. 2(b), on the graphite electrode, the voltammograms are essentially similar to those on the stainless steel electrode. But the potential gap between nucleation and dissolution on the graphite electrode is higher than that on the stainless steel electrode and, the electroplating limiting diffusing current density at the scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$ on the graphite electrode is lower than that on the stainless steel electrode. Therefore, using stainless steel as the negative electrode may result in higher voltage efficiency at lower charge-

discharge rate. Stainless steel materials are of low cost and can be easily prepared. Moreover, using of stainless steel as the negative electrode, the weight and volume of the battery can be greatly reduced.

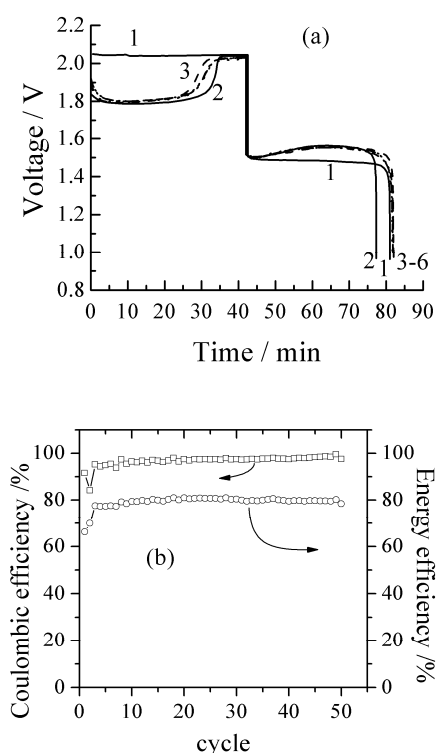


FIG. 3 CHARGE-DISCHARGE PROFILES DURING CHARGE-DISCHARGE CYCLES OF STAINLESS STEEL-TAC BATTERY SYSTEM IN $1.5 \text{ mol}\cdot\text{L}^{-1} \text{ Pb}(\text{BF}_4)_2 + 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HBF}_4$ AQUEOUS SOLUTION, (a) CHARGE-DISCHARGE PROFILE OF THE 1ST-6TH CHARGE-DISCHARGE CYCLE, (b) CYCLIC PERFORMANCE

Using TaC as the positive electrode and stainless steel as the negative electrode, a small laboratory cell was fabricated and tested. Typical charge-discharge profiles of the battery are shown in Fig. 3, in which the electrolyte adopted is $1.5 \text{ mol}\cdot\text{L}^{-1} \text{ Pb}(\text{BF}_4)_2 + 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ HBF}_4$ and the current density adopted is $10 \text{ mA}\cdot\text{cm}^{-2}$. During the first cycle, the charge voltage exceeds 2.0 V , the average discharge voltage is about 1.48 V and the coulombic efficiency is 91.6% (Fig. 3(a)). The charge voltage declines noticeably in the subsequent cycles since the formation of PbO on the surface of the positive electrode, which is consistent with the literature [12-17]. The average discharge voltage is about 1.55 V after the first cycle, which is a little higher than that of the first charge-discharge cycle, and might be attributed to more compacted and higher coverage of PbO_2 and Pb sediments deposited on the electrode surface. The coulombic efficiency of above 96% and an average energy efficiency of about 80.2% are obtained after the sixth charge-discharge cycles, as can be seen from Fig. 3(b).

The electrochemical performance of the stainless steel-TaC all-lead redox flow battery in different concentrations of $\text{Pb}(\text{BF}_4)_2$ in $1.0 \text{ mol}\cdot\text{L}^{-1}$ HBF_4 was evaluated. The coulombic efficiency increases as the current density and the electrolyte concentration increase. The battery can offer an energy efficiency of above 70% at the current density of $20 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than that of the all-lead redox flow battery in aqueous methanesulfonic acid ^[12-19] (about 65% at $\sim 20 \text{ mA}\cdot\text{cm}^{-2}$). The battery in $1.5 \text{ mol}\cdot\text{L}^{-1}$ $\text{Pb}(\text{BF}_4)_2 + 1 \text{ mol}\cdot\text{L}^{-1}$ HBF_4 can offer a maximum energy efficiency of 80.2% at the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than that shown in our previous work ^[20]. The stainless steel-TaC all-lead redox flow battery has a higher average voltage efficiency and a higher average energy efficiency at the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. These are consistent with the CVs.

Conclusions

In the present work, stainless steel as the negative electrode and TaC as the positive electrode are proposed for the all-lead redox flow battery in the intermixture of $\text{Pb}(\text{BF}_4)_2$ and HBF_4 aqueous electrolyte. The performance of the all-lead redox flow battery is improved comparing with graphite as the positive and negative electrode. The miniature battery can offer an average discharge voltage of 1.55 V, an average coulombic efficiency of above 96%, and an energy efficiency of above 70% at the current density of $20 \text{ mA}\cdot\text{cm}^{-2}$. The battery in $1.5 \text{ mol}\cdot\text{L}^{-1}$ $\text{Pb}(\text{BF}_4)_2 + 1 \text{ mol}\cdot\text{L}^{-1}$ HBF_4 can offer a maximum energy efficiency of above 80.2% at the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than that shown in our previous work.

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